

LETTER TO THE EDITOR

Diffuse interstellar bands in fullerene planetary nebulae: the fullerenes - diffuse interstellar bands connection

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ABSTRACT

We present high-resolution ($R \sim 15,000$) VLT/UVES optical spectra of two planetary nebulae (PNe; Tc 1 and M 1-20) where C_{60} (and C_{70}) fullerenes have already been found. These spectra are of high-quality ($S/N > 300$) for PN Tc 1, which permits us to search for the expected electronic transitions of neutral C_{60} and diffuse interstellar bands (DIBs). Surprisingly, we report the non-detection of the most intense optical bands of C_{60} in Tc 1, although this could be explained by the low C_{60} column density estimated from the C_{60} infrared bands if the C_{60} emission peaks far away from the central star. The strongest and most common DIBs in both fullerene PNe are normal for their reddening. Interestingly, the very broad 4428 Å DIB and the weaker 6309 Å DIB are found to be unusually intense in Tc 1. We also report the detection of a new broad (FWHM ~ 5 Å) unidentified band at ~ 6525 Å. We propose that the 4428 Å DIB (probably also the 6309 Å DIB and the new 6525 Å band) may be related to the presence of larger fullerenes (e.g., C_{80} , C_{240} , C_{320} , and C_{540}) and buckyonions (multishell fullerenes such as $C_{60}@C_{240}$ and $C_{60}@C_{240}@C_{540}$) in the circumstellar envelope of Tc 1.

Key words. Astrochemistry — Line: identification — circumstellar matter — ISM: molecules — planetary nebulae: individual: Tc 1, M 1-20

1. Introduction

The diffuse interstellar bands (DIBs) have remained a mystery for astronomers since their discovery about ninety years ago (Heger 1922); they are one of the long-standing problems in the interstellar medium (ISM). Nowadays, more than 400 DIBs have been identified in the ISM (e.g., Hobbs et al. 2008; Geballe et al. 2011). No DIB carrier has been convincingly identified, although more recent studies suggest that the DIB carriers may be complex molecules containing carbon (see e.g., Herbig 1995; Snow & McCall 2006; Cox 2011). Polycyclic aromatic hydrocarbons (PAHs; e.g., Salama et al. 1999), fullerenes (e.g., Foing & Ehrenfreund 1994; Herbig 2000; Iglesias-Groth 2007), and polyatomic organic molecules (e.g., Maier et al. 2011) are among the proposed DIB carriers. In particular, the fullerenes - DIB hypothesis may also explain the intense UV absorption band at 217 nm as due to fullerene-based molecules such as buckyonions (multishell fullerenes) (e.g., Iglesias-Groth 2004) and hydrogenated fullerenes (e.g., Cataldo & Iglesias-Groth 2009).

The 9577 and 9632 Å DIBs observed in a few hot reddened stars lie near two electronic transitions of the C_{60} cation observed in rare gas matrices (Foing & Ehrenfreund 1994). However, the presence of fullerenes in astrophysical environments has been a matter of debate until recently when Spitzer observations have provided evidence for C_{60} and C_{70} fullerenes from planetary nebulae (PNe; Cami et al. 2010; García-Hernández et al. 2010, 2011a, 2012a), reflection nebulae (Sellgren et al. 2010) and the least H-deficient R Coronae Borealis (RCB) stars (García-Hernández et al. 2011b,c). None of these environments is highly

hydrogen-deficient. Furthermore, the recent detection of C_{60} fullerenes in PNe with normal H-abundances (García-Hernández et al. 2010, 2011a, 2012a) suggests that large fullerenes may be formed as decomposition products of hydrogenated amorphous carbon (HAC) dust and that fullerenes may be not so exotic and can form under conditions that are common to essentially all solar-like stars at the end of their lives.

Thus, fullerenes and related large carbon-based species (e.g., other fullerenes as stable exohedral or endohedral metallo-complexes; Kroto & Jura 1992) might be ubiquitous in the ISM and continue to be serious candidates for DIB carriers (e.g., Bettens & Herbst 1996; Herbig 1995; Iglesias-Groth 2007). However, a detailed analysis of the DIBs towards fullerene-containing - accompanied or not by PAH molecules (e.g., García-Hernández et al. 2012b) - astrophysical environments is mandatory before one can reach conclusions about the nature of the DIB carriers. In this context, the recent infrared detection of large fullerenes in PNe offers the beautiful opportunity for studying the DIB spectrum of sources where fullerenes are abundant. In this *Letter* we present for the first time a detailed inspection of the optical spectra of two fullerene PNe, which permits us to directly explore the fullerenes - DIB connection.

2. Optical VLT/UVES spectroscopy of fullerene PNe

We acquired optical spectra of the fullerene PNe Tc 1 ($B=11.1$, $E(B-V)=0.23$; Williams et al. 2008) and M 1-20 ($B=13.7$, $E(B-V)=0.80$; Wang & Liu 2007). Tc 1 displays a fullerene-dominated spectrum with no clear signs of PAHs while M 1-20 also shows PAH features (García-Hernández et al. 2010). The

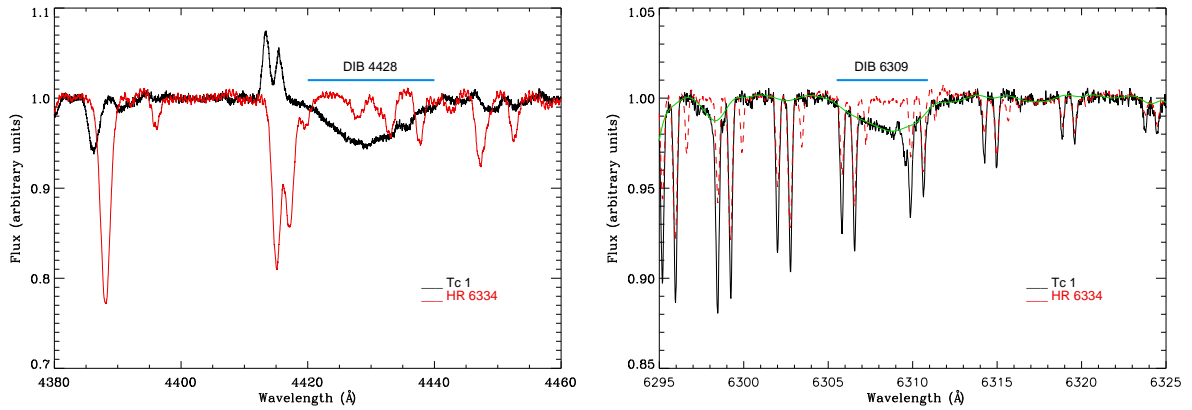


Fig. 1. Spectra of Tc 1 (in black) and HR 6334 (in red) around the 4428 Å (left panel) and 6309 Å DIBs (right panel). Both DIBs are found to be unusually strong in Tc 1 while HR 6334 - with a higher $E(B-V)$ of 0.42 - does not show evidence of their presence. The telluric line corrected spectrum of Tc 1 around 6309 Å (right panel) is shown by the smooth line (in green).

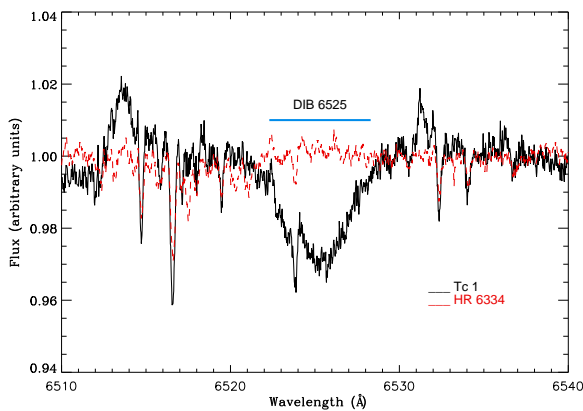


Fig. 2. Spectral region around the new broad unidentified band at 6525 Å in Tc 1 (in black) and HR 6334 (in red).

observations were carried out at the ESO VLT (Paranal, Chile) in service mode between May and September 2011. The optical spectra were taken in the wavelength ranges ~ 3300 -4500, 5750-7500, and 7700-9400 Å with UVES at the UT2 telescope using the 2.4" slit with the standard setting DIC2 (390+760). This configuration gives a resolving power of $\sim 15,000$ and an adequate interorder separation. We required $R \sim 15,000$ to appropriately sample the relatively broad C_{60} features together with the generally narrower DIBs (e.g., 5797, 5850, 6196, 6614 Å). To detect weak broad (≥ 4 Å) C_{60} features in the optical we aimed for a minimum signal-to-noise (S/N) ratio of 200 around 3760 Å.

As comparison stars for Tc 1 we selected the nearby B-type star HR 6334 ($B=5.1$; $E(B-V)=0.42$; Wegner 2003) and for M 1-20 HR 6716 ($B=5.7$; $E(B-V)=0.22$; Wegner 2003). Both comparison stars were observed on the same dates as the corresponding PNe using the same VLT/UVES set-up. The observed spectra were processed by the UVES data reduction pipeline (Ballester et al. 2000) and the stellar continuum was fitted by using standard astronomical tasks in IRAF.

For Tc 1, we obtained 10-12 individual exposures (of 900 s each) in the ~ 3300 -4500, 5750-7500, and 7700-9400 Å spectral ranges, giving total exposure times of 2.5-3 hours. The S/N in the continuum in the summed Tc 1 spectrum is ~ 300 at 4000 Å and higher than 350 at wavelengths longer than 6000 Å. For the

fainter PN M 1-20, however, we only could obtain eight individual exposures of 1800 s each in both ~ 5750 -7500 and 7700-9400 Å spectral regions, giving a total exposure time of four hours. The S/N in the individual 1800 s exposures in the blue region (3300-4500 Å) was too low (< 10). During the execution of our service program we decided to use a binning 2x2 to increase the S/N around 4000 Å but we only obtained two individual exposures of 1800 s each. Thus, the S/N in the continuum in the best M 1-20 spectra is ~ 20 at 4000 Å and higher than 30 at wavelengths longer than 6000 Å. Finally, an S/N in excess of 450 was easily achieved in the summed spectra of the bright comparison stars HR 6334 and HR 6716 by using total exposure times of several minutes.

Unfortunately, the S/N in the M 1-20 spectrum is too low to search for weak and broad absorption bands (e.g., neutral C_{60} features, see below) in its spectrum but it was found to be enough to detect and characterize several of the strongest and most common DIBs towards this PN with a rather high $E(B-V)$ of 0.80.

3. Electronic transitions of neutral C_{60}

We have searched the high-quality (S/N >300) spectra of the PN Tc 1 (see above) for electronic transitions of C_{60} .¹ The strongest electronically allowed transitions of neutral gas-phase C_{60} molecules, as measured in the laboratory, are located around ~ 3760 , 3980, and 4024 Å with widths of 8, 6, and 4 Å (Sassara et al. 2001; see also García-Hernández et al. 2012b). The strongest C_{60} transition seen in the laboratory spectra is that at 3980 Å (Sassara et al. 2001).

Surprisingly, we can find no evidence for the presence of neutral C_{60} in absorption (or emission) at the wavelengths of the expected electronic transitions mentioned above. This is shown in Fig. A1 (in the appendix) where we compare the Tc 1 velocity-corrected spectra² with those of the nearby B-type star HR 6334 around the expected positions of the strongest C_{60} transitions. It is to be noted here that the 3760 and 4024 Å bands coincide with several strong O lines and He I 4026 Å line, respectively, which hampers the identification of broad and weak

¹ C_{70} is ten times less abundant than C_{60} (e.g., García-Hernández et al. 2012a) and we do not find evidence for extra absorption around (± 10 Å) the expected C_{70} electronic transitions (e.g., Ajje et al. 1990).

² We applied average velocity corrections of -105.8 km s $^{-1}$ (~ -1.4 Å) for Tc 1 and of 20.1 km s $^{-1}$ (~ 0.3 Å) for HR 6334.

absorption features. However, the spectral region around 3980 Å (Fig. A1 in the appendix, right panel) is free from any contaminant and there is no evidence for the presence of the neutral C₆₀ feature at this wavelength.

The one-sigma detection limits on the equivalent widths (EQWs) derived from our Tc 1 spectra are 63, 20, and 12 mÅ for the 3760, 3980, and 4024 Å C₆₀ transitions³. This translates into column densities of 6×10^{12} , 1×10^{13} , and 6×10^{12} cm⁻². We can compare this column density limit of about 10^{13} cm⁻² with estimates of the circumstellar density of C₆₀ molecules, taking into account the total number of C₆₀ molecules ($N(C_{60}) = 1.8 \times 10^{47}$ for $d = 2$ kpc; García-Hernández et al. 2011a) calculated from the IR C₆₀ features. By following García-Hernández et al. (2012b) (Equations 1, 2, and 3), we can estimate the density of C₆₀ molecules by assuming a spherical shell of radius ($R_{out} - R_{in}$) and a uniform number of C₆₀ molecules throughout the shell. Thus, considering that $L = 1480 L_{\odot}$ for Tc 1 (Pottasch et al. 2011), we obtain dust temperatures (T_d) of 415 K at ~ 18 au and 100 K at 301 au, where the first temperature is the C₆₀ excitation temperature (García-Hernández et al. 2011a) and the latter temperature corresponds to the minimum temperature of the dust to be detected in the mid-IR by Spitzer. For a distance of 2 kpc, we estimate a circumstellar density of fullerenes $n(C_{60}) = 0.46$ cm⁻³ and a C₆₀ column density along the path ($R_{out} - R_{in}$) of $\sim 2 \times 10^{15}$ cm⁻²; a lower C₆₀ column density of 3×10^{14} cm⁻² is obtained for $L = 10^4 L_{\odot}$. Thus, our estimate of the C₆₀ column density is 200–300 times higher than the observed upper limits. It is to be noted here that although the Spitzer/IRS observations contain a marginal amount of spatial information ($\sim 2''/\text{pixel}$) and that mid-IR images at much higher spatial resolution would be desirable, Bernard-Salas et al. (2012) presented tentative evidence that the 8.5 μm emission (and attributed to C₆₀) in Tc 1 is extended and peaks at 2–3 pixels (~ 6400 – 9700 au for $d = 2$ kpc) from the central star. By assuming that fullerenes are uniformly distributed in a shell of $R_{out} = 9700$ au and $R_{in} = 6400$ au, the estimated C₆₀ column density ($\sim 1 \times 10^{12}$ cm⁻²) is a factor between 6 and 10 below our observed upper limits.

In short, our C₆₀ column density values estimated from the C₆₀ IR bands could explain the non-detection of the electronic C₆₀ transitions in our Tc 1's optical spectra only if the C₆₀ emission peaks far away from the central star. However, we cannot discard that the line of sight to Tc 1 may not intersect the fullerene-rich regions of the circumstellar shell (e.g., if the fullerenes may be formed in clumps). On the other hand, one can speculate that the strongest 3980 Å C₆₀ band - perhaps the other electronic bands, too - could be suppressed if the fullerenes are in the solid-state phase (e.g., Evans et al. 2012; García-Hernández et al. 2012a). However, a laboratory spectrum of solid-state C₆₀ in n-hexane displays the same transitions seen in the gas-phase (F. Cataldo, private communication). An alternative and more exotic explanation may be that the mid-IR features seen in Tc 1 are not due to C₆₀ and C₇₀ solely, being contaminated by other more complex fullerene-based molecules. This latter interpretation seems to be supported by our study of the DIBs towards Tc 1 and presented below.

4. Diffuse interstellar bands in fullerene PNe

We have followed the catalog of DIBs measured in the high-S/N HD 204287's spectrum (Hobbs et al. 2008) to search them in the VLT/UVES spectrum of Tc 1 and M 1-20. However, we concentrate here on analyzing eight of the strongest DIBs most commonly found in the ISM as well as on detecting unusually strong DIBs (i.e., not present in the nearby comparison stars and/or in Hobbs et al. 2008), which could be potentially due to fullerenes or fullerene-based molecules. Thus, we can compare the characteristic of most common DIBs for both PNe in our sample as well as with existing literature data on field-reddened stars (e.g., Luna et al. 2008). The exhaustive analysis of the weaker DIBs listed by Hobbs et al. (2008) and also detected in Tc 1's spectrum will be published elsewhere.

Our list of DIBs in Tc 1 and M 1-20 are listed in Table A1 (in the appendix), where we give the measured central wavelength, FWHM, EQW, the S/N in the neighboring continuum, and the normalized equivalent widths EQW/E(B-V). For comparison we also list the EQW/E(B-V) measured in HD 204827 and field-reddened stars by Hobbs et al. (2008) and Luna et al. (2008). It should be noted that we could not estimate the total absorption of the 6993 and 7223 Å DIBs (not shown in Table A1 in the appendix) in our PNe because of the strong meddling from the telluric lines. For the well-studied DIBs at 5780, 5797, 5850, 6196, 6270, 6284, 6380, and 6614 Å⁴, the EQW/E(B-V) in fullerene PNe agree reasonably well with the values reported in HD 204827 (Hobbs et al. 2008) and field-reddened stars (Luna et al. 2008). The observed nearby comparison stars HR 6334 and HR 6716 also display EQW/E(B-V) values completely consistent (within the errors) with those measured in our PNe. This indicates that the carriers of the latter well-studied DIBs are not particularly overabundant in fullerene PNe.

Interestingly, the well-studied DIB at 4428 Å as well as the weaker 6309 Å DIB listed by Hobbs et al. (2008) are found to be unusually strong towards Tc 1. These last DIBs are not detected in the nearby comparison star HR 6334 with a higher E(B-V) of 0.42. Fig. 1 compares the 4428 and 6309 Å DIBs in Tc 1 with those in HR 6334. Adopting a Lorentzian profile for the 4428 Å DIB (Snow et al. 2002), we obtain EQW=860 mÅ, which is at least a factor of two greater than expected for the low reddening of E(B-V)=0.23 in Tc 1; see e.g., Fig. 6 and 15 in Snow et al. (2002) and van Loon et al. (2012). We note that there is tentative evidence for an unusually strong (5–10% of the continuum and EQW=2579±786 mÅ) 4428 Å DIB in M 1-20, too (see Fig. A2 in the appendix), something that supports our finding in Tc 1. However, we prefer to be cautious until higher S/N M 1-20 spectra are obtained. On the other hand, the uncommon 6309 Å DIB in Tc 1 appears to be three times more intense than that observed in HD 204287 by Hobbs et al. (2008) (see Table A1 in the appendix). Finally, an unidentified broad feature at 6525 Å (FWHM ~ 5 Å, EQW=173 mÅ) is detected in the Tc 1 spectrum (Fig. 2). Fig. 2 shows that the 6525 Å band is real because it is not detected in the spectrum of the comparison star HR 6334 taken with the same UVES setup and at the same time.

³ One-sigma detection limits for the EQWs in our spectra scale as $\sim 1.064 \times \text{FWHM} / (S/N)$ (see e.g., Hobbs et al. 2008) but this value for the 3760 Å band is estimated by modeling and subtracting the oxygen lines around 3760 Å.

⁴ Note that a possible exception is the 6284 Å DIB but its strength is known to be not very well correlated with the interstellar reddening (e.g., Luna et al. 2008).

5. Fullerenes - DIB connection

Our finding of an unusually strong 4428 Å DIB towards Tc 1 (see left panel of Fig. 1) necessarily prompts the idea that the 4428 Å DIB carrier may be related with fullerenes or fullerene-based molecules (Iglesias-Groth 2007). Remarkably, photo-absorption theoretical models of several large fullerenes such as C₈₀, C₂₄₀, C₃₂₀, and C₅₄₀ predict their strongest transitions very close in wavelength (± 10 Å) to this 4428 Å DIB (Iglesias-Groth 2007)⁵. The theoretical spectra of several multishell fullerenes (buckyonions such as C₆₀@C₂₄₀ and C₆₀@C₂₄₀@C₅₄₀) reported by Iglesias-Groth (2007) also display a strong 4428 Å band. In this context, the broad 4428 Å band may be well explained by the superposition of the transitions of fullerenes bigger than C₆₀ and buckyonions. This would be consistent with the recent exhaustive study of the 4428 Å DIB by van Loon et al. (2012), which suggests the carrier to be a large, compact, and neutral molecule that is relatively resistant to impacting energetic photons or particles.

Another interesting feature is that our Tc 1 spectra also lack the unidentified 4000 Å band (see Fig. A1 in the appendix) that is detected in the RCB star DY Cen (García-Hernández et al. 2012b). García-Hernández et al. (2012b) suggested that the mid-IR features at ~ 7.0 , 8.5, 17.4, and 18.8 μm and the unidentified 4000 Å band in DY Cen are likely due to proto-fullerenes (PFs) or fullerene precursors rather than to C₆₀. Interestingly, DY Cen displays a 'normal' 4428 Å DIB, supporting the claim that fullerenes and fullerene-based molecules such as buckyonions are not especially overabundant toward DY Cen. Thus, the unusually strong 4428 Å DIB and the lack of the unidentified 4000 Å band in Tc 1 may indicate an efficient conversion of PFs to fullerenes and fullerene-based molecules in its circumstellar envelope (see e.g., Duley & Hu 2012).

Furthermore, the apparent lack of the strongest electronic transitions of the C₆₀ molecule in Tc 1 may indicate that we are not seeing emission from isolated, free C₆₀ molecules, which would explain the variable properties of the mid-IR C₆₀ spectral features observed in fullerene PNe (Bernard-Salas et al. 2012; García-Hernández et al. 2012a). At present, the HAC's photochemical processing is the most likely C₆₀ formation route in the complex circumstellar envelopes of PNe (García-Hernández et al. 2012a; Bernard-Salas et al. 2012; Micelotta et al. 2012). Larger fullerenes may grow from pre-existing C₆₀ molecules (Dunk et al. 2012) that may be supplied by the photochemical processing of HAC dust, opening the possibility of forming other fullerene-based molecules such as buckyonions and fullerene adducts. Indeed, fullerenes and PAHs may be mixed in the circumstellar envelopes of fullerene PNe (e.g., M 1-20) and fullerene/PAH adducts may form via Dies-Alder cycloaddition reactions (García-Hernández et al. 2013).

Fullerene clusters or fullerene-based molecules such as buckyonions, fullerene/PAH adducts may still be excited by stochastic heating (e.g., from UV photons) emitting through the same IR vibrational modes. Indeed, very recent laboratory work demonstrates that fullerene/PAH adducts - such as C₆₀/anthracene Diels-Alder adducts - display mid-IR features strikingly coincident with those from C₆₀ and C₇₀ (García-Hernández et al. 2013). Unfortunately, the synthesis of multishell fullerenes (buckyonions) in the laboratory is challenging because their insolubility does not permit us to extract and sepa-

rate these species from the carbon soot in which they are present in small amounts (F. Cataldo, private communication).

In summary, we propose that the 4428 Å DIB (possibly also the 6309 Å DIB and the new 6525 Å band) is probably related to fullerenes bigger than C₆₀ (e.g., C₈₀, C₂₄₀, C₃₂₀, and C₅₄₀) and buckyonions (e.g., C₆₀@C₂₄₀, C₆₀@C₂₄₀@C₅₄₀) in the Tc 1 circumstellar environment. This possible fullerenes - DIB connection was previously suggested by Iglesias-Groth (2007) from theoretical considerations.

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⁵ The same models do not predict a 4428 Å band for the C₆₀ fullerene, in agreement with fullerene laboratory spectroscopy (e.g., Sassara et al. 2001).

Appendix A: Figures A1 and A2 and Table A1

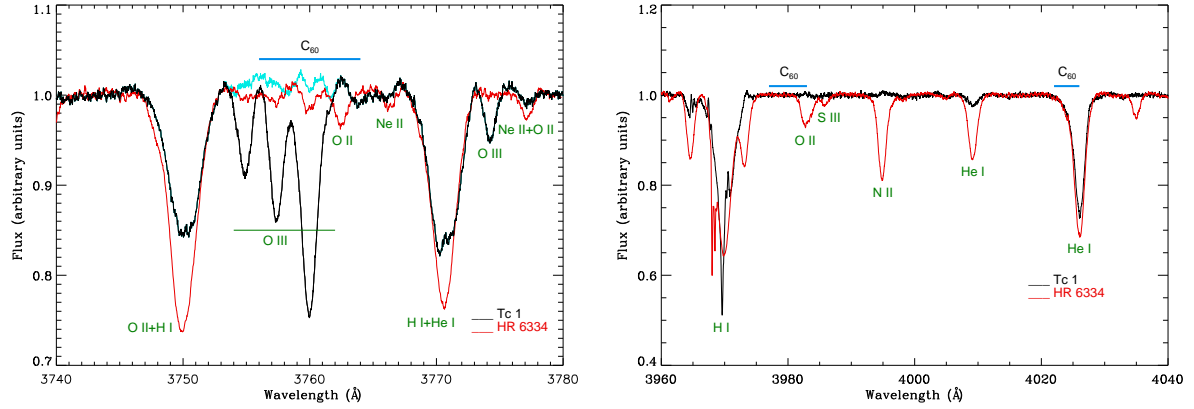


Fig. A.1. Velocity-corrected spectra of Tc 1 (in black) and HR 6334 (in red) around 3760 Å (left panel) and 4000 Å (right panel) where the atomic line identifications are indicated (in green). The expected positions (and FWHMs) of the C_{60} features are marked on top of the spectra. There is no evidence (additional absorption) in Tc 1 for the neutral C_{60} features at 3760, 3980, and 4024 Å. The residual spectrum (in cyan) obtained by subtracting the oxygen lines around 3760 Å is also shown.

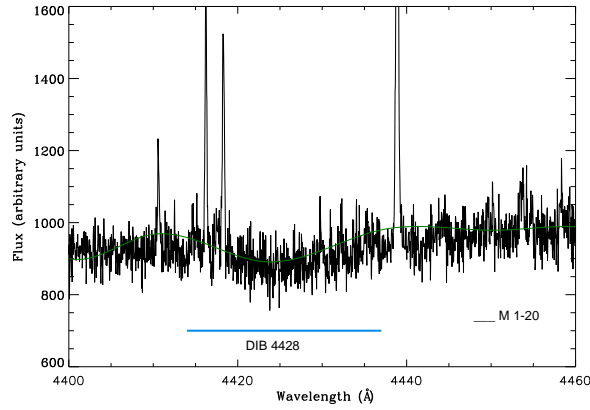


Fig. A.2. Spectrum of M 1-20 (in black) around the broad 4428 Å DIB. A heavily smoothed and emission line corrected spectrum is also overplotted (in green).

Table A.1. Diffuse interstellar bands in fullerene PNe.^a

Tc 1	M 1-20									Hobbs et al.	Luna et al.
λ_c	FWHM	EQW	S/N	EQW/ E_{B-V}	λ_c	FWHM	EQW	S/N	EQW/ E_{B-V}	EQW/ E_{B-V}	EQW/ E_{B-V}
(Å)	(Å)	(mÅ)		(Å/mag)	(Å)	(Å)	(mÅ)		(Å/mag)	(Å/mag)	(Å/mag)
4428.10 ^b	19.35	860	329	3.74	4426.56 ^b	19.94 ^c	2579 ^c	20 ^d	3.22	1.10	...
5780.40	2.06	105	416	0.46	5780.66	2.17	359	32	0.45	0.23	0.46
5796.88	0.99	42	357	0.18	5797.31	1.14	155	53	0.19	0.18	0.17
5849.60	1.35	11	346	0.047	5850.02	1.23	70	37	0.087	0.086	0.061
6195.85	1.17	13	549	0.056	6196.18	0.95	36	68	0.045	0.034	0.053
6269.77	1.93	9	548	0.037	6270.19	2.48	130	66	0.16	0.069	...
6283.93	4.91	316	579	1.38	6283.77	5.25	706	61	0.88	0.41	0.90
6308.90	2.98	42	530	0.18	0.049	...
6379.08	1.39	12	513	0.050	6379.56	1.30	93	56	0.12	0.085	0.088
6525.15	4.79	173	522	0.75
6613.50	1.42	36	412	0.16	6613.78	1.23	167	77	0.21	0.149	0.21

Notes.

^(a) The $3\text{-}\sigma$ errors in the EQWs scale like $\sim 3 \times \text{FWHM}/(\text{S/N})$ while we estimate that the FWHMs in Tc 1 are precise to the 0.03 Å level (less for M 1-20).

^(b) The characteristics of this DIB are estimated by adopting a Lorentzian profile (see e.g., Snow et al. 1992).

^(c) Best estimates found by clipping out the narrow emission lines and smoothing the spectrum with boxcar 15. The error in the quoted EQW is estimated to be ~ 786 mÅ.

^(d) S/N in the original spectrum.